

[JP,2000-034503,A]

Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the after alloy powder for Sm-Fe-N system bond magnets by which the particle surface was covered by the protective layer and in which oxidation resistance is improved and high magnetic properties are moreover realized in more detail about the after alloy powder for Sm-Fe-N system bond magnets.

[0002]

[Description of the Prior Art]The bond magnet which fabricated the powder of the hard magnetic material using the binder is used as various permanent magnet materials, such as a motor, a speaker, a microphone, and a sized generator. Corresponding to the miniaturization of apparatus in recent years, and a high increase in power, the rare earth alloy magnet material in which the hard magnetic material used also has high magnetic properties is used.

[0003]It uses it as a Sm-Fe-N system alloy, and is pulverized. [ the after alloy powder for Sm-Fe-N system bond magnets which is one of the rare earth alloy magnet materials ] [ the Sm-Fe system alloy obtained by processes, such as a casting process, a quenching method, and reduction diffusion method, ] Pulverizing, the coercive force manifestation mechanism of this Sm-Fe-N system magnet is a new creation type.

It is because it is necessary to pulverize to the diameter of a single domain particle in order to enlarge a \*\*\*\* mosquito.

[0004]

[Problem(s) to be Solved by the Invention]Generally, a rare earth alloy magnet material oxidizes easily from using a rare earth element as an ingredient, and magnetic properties fall by oxidation. Since the after alloy powder for Sm-Fe-N system bond magnets which is a rare earth alloy magnet material is also especially impalpable powder, it appears notably. For this reason, it oxidizes by the heating process in the case of bond magnet manufacture, and handling, and magnetic properties deteriorate greatly, and by the time it harnesses in the maximum the outstanding magnetic properties which a Sm-Fe-N system alloy has, it will not have resulted.

[0005]In the after alloy powder for rare earth bonded magnets of a Sm-Co system or a Nd-Fe-B system which is other rare earth alloy magnet materials, in order to improve corrosion resistance, various proposals are made. . For example, perform chemical conversion, such as phosphate treating and chromate treatment, on the powder surface. . Vapor-deposit (for example, JP,1-14902,A), zinc, and aluminum. Art, such as forming (for example, JP,64-15301,A) and a polymers coat (for example, JP,4-257202,A) and carrying out metal plating (for example, JP,7-142246,A), is proposed.

[0006]However, even if it applies the method of one of the above to the after alloy powder for Sm-Fe-N system bond magnets, oxidation resistance improves, but it will be ruined and magnetic properties will deteriorate. Since it is necessary to make it about several 10-micrometer thickness in order to acquire oxidation-resistant effect sufficient as a coat, the volume fraction of the material which reveals magnetic properties will fall, and the fall of magnetic properties will be caused.

[0007]In the method of one of the above, since condensation of impalpable powder also

takes place when forming a coat, the direction of magnetic anisotropy becomes irregular and the fall of magnetic properties is not avoided.

[0008]Then, this invention solves an aforementioned problem, cover the particle surface of after alloy powder with a stable and specific protective layer with few defects, such as a hole, thermally, and oxidation resistance is improved, And it aims at providing the after alloy powder for Sm-Fe-N system bond magnets in which high magnetic properties are realized when it is considered as a magnet by controlling condensation of impalpable powder.

[0009]

[Means for Solving the Problem]After alloy powder for Sm-Fe-N system bond magnets of this invention which solves an aforementioned problem was covered with a protective layer by which the particle surface is constituted from either a fluorine compound coat, a polysilazane cured film, an oxidized silicon coat or a silicon nitride film. A foundation layer may be formed under a protective layer.

[0010]A Sm-Fe-N system alloy used for this invention is obtained by performing nitriding treatment to a Sm-Fe system alloy which has a main phase of a hexagonal system. As for alloy composition, Sm is 20 to 30 % of the weight, nitrogen is 1 to 5 % of the weight, and Fe occupies the remainder. Without spoiling magnetic properties, a part of Fe may be replaced by Co in order to improve temperature characteristics.

[0011]Said Sm-Fe system alloy is manufactured by casting process, quenching method, reduction diffusion method, etc. It may heat-treat before a nitriding step in order to grow up a main phase of a hexagonal system in an alloy. In order to perform nitriding treatment efficiently, it is desirable to use an alloy as a granular material. In this case, particle diameter of a granular material also affects a pulverizing process after nitriding treatment, and, as for that size range, 20-63 micrometers is desirable. Although form of a grinder used for grinding of an alloy is not asked, in order to prevent oxidation of an alloy powder, it is desirable to have the structure which can grind in an inert atmosphere.

[0012]In a nitriding step of a Sm-Fe system alloy, heat treatment for diffusing homogeneously grinding by removal of adsorption gas of an alloy particle surface and hydrogen gas processing and nitrogen inside after alloy powder along with it may be performed.

[0013]Before a granular material after nitriding is fabricated as a bond magnet, it is desirable to pulverize to mean particle diameter of several micrometers. In order to pulverize a Sm-Fe-N system alloy, wet milling using an organic solvent or dry grinding under minute amount oxygen environment can be performed. Respectively publicly known various grinders can be used and grinding form in particular is not restricted.

[0014]When a protective layer is a fluorine compound coat, desirable average thickness is 0.1-0.2 micrometer. Although the fluorine compound can use a publicly known thing, it is desirable for cold cure 150 °C or less to be possible. It is because an organization of a Sm-Fe-N system alloy will change and degradation of magnetic properties will be caused, if a tunic is formed at an elevated temperature over 150 °C. It is desirable that it is solvent soluble. It is because film formation from a solution is possible and a tunic can be uniformly formed in the powder surface.

[0015]In order to form in a particle surface of after alloy powder for Sm-Fe-N system bond magnets a protective layer which comprises a fluorine compound coat, it can carry out by spraying a solvent which dissolved a fluorine compound, for example, making

after alloy powder stir with an agitator at a room temperature. It is preferred to make inside of an agitator into 0.1-1 vol% oxygen gas atmosphere at this time. It is because efficient coat formation will become difficult, or oxidation and organization change of a Sm-Fe-N system alloy will be caused and magnetic properties will be reduced, if the amount of oxygen is out of said range.

[0016]An agitator is heated at 100-150 °C after spraying for example, by a heating rate of 1-3 °C / min. In order to reconcile control of uniform and precise coat formation and a magnetic-properties fall, it carries out on condition of a suitable heating rate and calcination temperature.

[0017]When a protective layer is a polysilazane cured film, polysilazane can use a publicly known thing, but it is desirable for cold cure 150 °C or less to be possible. It is because an organization of a Sm-Fe-N system alloy will change and degradation of magnetic properties will be caused, if a tunic is formed at an elevated temperature over 150 °C. It is desirable that it is solvent soluble. It is because film formation from a solution is possible and a tunic can be uniformly formed in the powder surface.

[0018]In order to carry out polysilazane cured film formation, it carries out to a particle surface of after alloy powder for Sm-Fe-N system bond magnets by spraying a solvent which dissolved polysilazane, for example, making Sm-Fe-N system alloy impalpable powder stir within an agitator at a room temperature. As for an agitator to be used, what can give a shear mosquito to those with two or more sheets and an alloy powder with big stirring feather rotated at a high speed of 6 or more m/s of peripheral speed is desirable. It is because impalpable powder will condense at the time of coat formation and magnetic properties will be reduced as a result, if a shear mosquito is weak.

[0019]When stirring, it is preferred to make inside of an agitator into 0.1-1 vol% oxygen gas atmosphere. It is because efficient coat formation will become difficult, or oxidation and organization change of a Sm-Fe-N system alloy will be caused and magnetic properties will be reduced, if the amount of oxygen is out of said range.

[0020]An agitator is heated at 100-150 °C after spraying for example, by a heating rate of 1-3 °C / min. In order to reconcile control of uniform and precise coat formation and a magnetic-properties fall, it carries out on condition of a suitable heating rate and calcination temperature.

[0021]When a protective layer is an oxidized silicon coat or a silicon nitride film, desirable average thickness is 0.01-0.1 micrometer. Formation of a coat can be performed, for example by sputtering process. A sputtering system will not be limited especially if an insulating material can be used as a target.

[0022]When forming an oxidized silicon coat, a SiO<sub>2</sub> target is used for a target material, and it is 0.1-10 vol% oxygen-argon mixed gas atmosphere, When forming a silicon nitride tunic, using a SiN<sub>4</sub> target, it is 0.1-10 vol% nitrogen-argon mixed gas atmosphere, and reactive sputtering is performed. It is because a coat formation speed falls and membranes cannot be efficiently formed, if it is easy to produce a defect in a coat formed as concentration of oxygen in atmosphere or nitrogen is less than [ 0.1 vol% ] and 10 vol% is exceeded.

[0023]

[Example]Example 1 ... 1100 °C and heat treatment of 24 hours were performed into the Sm-Fe system (25-% of the weight Sm) alloy produced by the casting process by the high frequency dissolution in argon gas atmosphere. This heat-treated alloy was ground and it

was considered as 20-63-micrometer alloy coarse powder. 250 °C and heat treatment of 2 hours were performed for this alloy coarse powder in hydrogen gas atmosphere. Then, the inside of a furnace was replaced by a nitrogen gas atmosphere, and 480 °C and heat treatment of 72 hours were performed. The inside of a furnace was replaced by argon gas atmosphere, and 480 °C and heat treatment of 24 hours were performed. The Sm-Fe-N system alloy coarse powder produced by heat-treating in this way was ground by the vibration ball mill using drying ethanol as a solvent, and it was considered as the impalpable powder whose mean particle diameter is about 4 micrometers.

[0024] Making the above-mentioned impalpable powder stir within the agitator of the nitrogen-oxygen mixed gas atmosphere of 0.1 vol% oxygen, the fluorine compound solution was dropped so that it might become the amount of fluorine compounds 1% of the weight to the amount of impalpable powder. The high-speed-stirring machine (the product made from Fukae Industry, a trade name: high speed mixer FS-1) was used for the agitator at the fluorine compound using the amorphous-fluorocarbon-resin solution (the Asahi Glass [ Co., Ltd. ] make, a trade name: SAITOPPU).

[0025] Temperature up was carried out to 150 °C by 1 °C / min after dropping, after holding at the temperature for 2 hours, it cooled, and the fluorine compound coat was formed.

[0026] About the impalpable powder in which the tunic was formed, it held in the homoiothermal highly humid tub of 65 °C and 90%RH for 1000 hours, the magnetic properties before and behind that were compared, and the heat characteristic was investigated. Magnetic properties mixed impalpable powder with paraffin, and measured what was fabricated all over the magnetic field of 20kOe with the oscillating sample type flux meter (VSM). Demagnetizing field amendment was not carried out in this measurement. A result is shown in Table 1.

[0027] Example 2 ... It was dropped so that it might become the amount of fluorine compounds 2% of the weight to the amount of impalpable powder which used the fluorine compound solution in Example 1, and also the fluorine compound coat was formed like Example 1, and the same evaluation as Example 1 was carried out. A result is shown in Table 1.

[0028] Comparative example 1 ... The same evaluation as Example 1 was carried out about the impalpable powder before forming the fluorine compound tunic obtained in Example 1. A result is shown in Table 1.

[0029] Example 3 ... the Sm-Fe system (25-% of the weight Sm) alloy powder produced with reduction diffusion method -- 35 vol% -- 480 °C and heat treatment of 6 hours were performed in ammonia gas hydrogen gas atmosphere. Then, the inside of a furnace was replaced by argon gas atmosphere, and 480 °C and heat treatment of 2 hours were performed. The Sm-Fe-N system after alloy powder produced by heat-treating in this way was pulverized with the jet mill which used nitrogen gas as the carrier, and was used as impalpable powder with a mean particle diameter of 3 micrometers.

[0030] Making the above-mentioned impalpable powder stir within the agitator of the nitrogen-oxygen mixed gas atmosphere of 0.1 vol% oxygen, the fluorine compound solution was dropped so that it might become the amount of fluorine compounds 1% of the weight to the amount of impalpable powder. The same thing as Example 1 was used for the fluorine compound and the agitator. Temperature up was carried out to 150 °C by 1 °C / min after dropping, after holding at the temperature for 2 hours, it cooled, and the

fluorine compound coat was formed.

[0031]About the impalpable powder in which the tunic was formed, the same evaluation as Example 1 was carried out. A result is shown in Table 1.

[0032]Comparative example 2 ... The same evaluation as Example 1 was carried out about the impalpable powder before forming the fluorine compound tunic obtained in Example 3. A result is shown in Table 1.

[0033]

[Table 1]

		磁気特性		
		飽和磁束 $4\pi M$ (kG)	保磁力 $H_c$ (kOe)	最大磁気球積 <sup>*</sup> -積 (BH) <sub>max</sub> (MGoe)
実施例 1	熱処理前	13.8	8.8	30.1
	熱処理後	13.7	8.2	27.8
実施例 2	熱処理前	13.6	8.8	28.9
	熱処理後	13.6	8.7	28.3
実施例 3	熱処理前	13.5	9.3	28.8
	熱処理後	13.6	9.0	27.9
比較例 1	熱処理前	14.0	8.7	31.2
	熱処理後	13.7	6.1	25.3
比較例 2	熱処理前	13.7	9.3	30.4
	熱処理後	13.0	4.8	24.8

[0034]Example 4 ... Making the impalpable powder used in Example 1 stir within the agitator of the nitrogen-oxygen mixed gas atmosphere of 0.1vol% oxygen, the polysilazane solution was dropped so that it might become the amount of polysilazane 1% of the weight to the amount of impalpable powder. Perhydropolysilazane (trade name: a Hervic low-temperature type, the N.E. CHEMCAT CORP. make) was used for polysilazane. The same thing as Example 1 was used for the agitator.

[0035]Temperature up was carried out to 150 \*\* by 3 \*\* / min after dropping, after holding at the temperature for 2 hours, it cooled, and the polysilazane cured film was formed.

[0036]About the impalpable powder in which the tunic was formed, it heat-treated at a 200 \*\* air furnace for 1 hour, the magnetic properties before and behind that were compared, and the heat characteristic was investigated. Magnetic properties were performed by the same method as Example 1. A result is shown in Table 2.

[0037]Example 5 ... It is the same method as Example 4, however the polysilazane solution was dropped so that it might become the amount of polysilazane 2% of the weight, and the polysilazane cured film was formed. About the impalpable powder in which the tunic was formed, the heat characteristic was investigated like Example 4. A

result is shown in Table 2.

[0038]Example 6 ... Sputtering of the impalpable powder used in Example 1 was carried out for 10 minutes with the sputtering system of the ion-guns method in the argon oxygen mixed gas atmosphere of 0.2vol% oxygen using the  $\text{SiO}_2$  target. Stirring impalpable powder was continued between sputtering. Thus, about the impalpable powder in which the oxidized silicon tunic was formed, the heat characteristic was investigated like Example 4. A result is shown in Table 2.

[0039]Example 7 ... It is the same method as Example 6, however sputtering time was carried out for 30 minutes, and the impalpable powder in which the oxidized silicon tunic was formed was obtained. About the obtained impalpable powder, the heat characteristic was investigated like Example 4. A result is shown in Table 2.

[0040]Example 8 ... Sputtering of the impalpable powder used in Example 1 was carried out for 30 minutes with the sputtering system of the ion-guns method in the argon nitrogen mixed gas atmosphere of 0.2vol% nitrogen using the  $\text{SiN}_4$  target. Stirring impalpable powder was continued between sputtering. Thus, about the impalpable powder in which the silicon nitride tunic was formed, the heat characteristic was investigated like Example 4. A result is shown in Table 2.

[0041]Example 9 ... Sputtering of the impalpable powder used in Example 3 was carried out for 30 minutes with the sputtering system of the ion-guns method in the argon oxygen mixed gas atmosphere of 0.2vol% oxygen using the  $\text{SiO}_2$  target. Stirring impalpable powder was continued between sputtering. Thus, about the impalpable powder in which the oxidized silicon tunic was formed, the heat characteristic was investigated like Example 4. A result is shown in Table 2.

[0042]Comparative example 3 ... The same evaluation as Example 4 was carried out about the impalpable powder before forming the polysilazane cured coating obtained in Example 4. A result is shown in Table 2.

[0043]

[Table 2]

		磁気特性		
		飽和磁束 $4\pi I_m$ (kG)	保磁力 $H_c j$ (kOe)	最大磁気エネルギー (BH) <sub>max</sub> (MGoe)
実施例 4	熱処理前	13.9	8.7	30.8
	熱処理後	13.1	7.2	25.1
実施例 5	熱処理前	13.7	8.7	29.5
	熱処理後	13.1	7.8	26.3
実施例 6	熱処理前	13.9	8.7	30.8
	熱処理後	13.1	7.2	25.1
実施例 7	熱処理前	13.7	8.7	29.5
	熱処理後	13.1	7.8	26.3
実施例 8	熱処理前	13.7	8.5	28.7
	熱処理後	13.0	7.5	25.2
実施例 9	熱処理前	13.2	9.2	29.3
	熱処理後	13.2	8.3	27.0
比較例 3	熱処理前	14.0	8.7	31.2
	熱処理後	5.7	1.7	0.8

[0044]According to this invention, the above result shows that the oxidation resistance of the after alloy powder for Sm-Fe-N system bond magnets is improved, and high magnetic properties are realized.

[0045]

[Effect of the Invention]By this invention, the particle surface of after alloy powder was thermally covered with the specific protective layer with stably few defects, such as a hole, oxidation resistance has been improved, and when it was considered as a magnet by moreover controlling condensation of impalpable powder, the after alloy powder for Sm-Fe-N system bond magnets in which high magnetic properties are realized was provided.

Claim(s)]

[Claim 1]After alloy powder for Sm-Fe-N system bond magnets by which a particle surface of a Sm-Fe-N system alloy was covered by a protective layer.

[Claim 2]The after alloy powder for Sm-Fe-N system bond magnets according to claim 1 in which said protective layer comprises a fluorine compound coat.

[Claim 3]The after alloy powder for Sm-Fe-N system bond magnets according to claim 1 in which said protective layer comprises a polysilazane cured film.

[Claim 4]The after alloy powder for Sm-Fe-N system bond magnets according to claim 1 in which said protective layer comprises an oxidized silicon coat.

[Claim 5]The after alloy powder for Sm-Fe-N system bond magnets according to claim 1

in which said protective layer comprises a silicon nitride film.

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